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ance Notes on Codes and Abbreviations" appearing at the begin-
ning of each regular issue of the PCT Gazette.

(54) Title: **SULPHUR PELLET COMPRISING H₂S-SUPPRESSANT**

(57) Abstract: The invention provides a sulphur pellet comprising at least one H₂S-suppressant. The invention further provides a process for the manufacture of sulphur pellets comprising at least one H₂S-suppressant, comprising the steps of: (a) mixing elemental sulphur, one or more H₂S suppressants and optionally a filler in a mixing unit to obtain a mixture; (b) shaping and/or pelletising the mixture obtained in step (a) in a pelletising unit to obtain H₂S-suppressant comprising sulphur pellets. The invention further provides a process for the manufacture of a sulphur-comprising asphalt paving mixture comprising the steps of: (i) preheating bitumen at a temperature of between 140 and 180 °C; (ii) preheating aggregate at a temperature of between 140 and 180 °C; (iii) mixing the hot bitumen with the hot aggregate in a mixing unit, wherein sulphur pellets comprising H₂S-suppressant according to the invention are added in at least one of the steps (i), (ii) or (iii). The invention also provides the use of a sulphur comprising asphalt paving mixture comprising H₂S suppressant in the paving of roads.

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SULPHUR PELLET COMPRISING H₂S-SUPPRESSANTFIELD OF THE INVENTION

The invention relates to a sulphur pellet. The invention further relates to a process for the manufacture of sulphur pellets. The invention also relates to a process for the manufacture of a sulphur-comprising asphalt paving mixture using sulphur pellets according to the invention.

BACKGROUND OF THE INVENTION

In the road construction and road paving industry, it is a well-practised procedure to coat aggregate material such as sand, gravel, crushed stone or mixtures thereof with hot fluid bitumen, spread the coated material as a uniform layer on a road bed or previously built road while it is still hot, and compact the uniform layer by rolling with heavy rollers to form a smooth surfaced road.

The combination of bitumen with aggregate material, such as sand, gravel, crushed stone or mixtures thereof, is also referred to as "asphalt". Bitumen, also referred to as "asphalt binder", is usually a liquid binder comprising asphaltenes, resins and solvents. Bitumen can for example comprise pyrogenous mixtures derived from petroleum residues such as residual oils, tar or pitch or mixtures thereof.

It is known in the art that sulphur can be mixed with bitumen for applications in the road construction and road paving industry. Efforts towards improving the addition of sulphur to bitumen are for example described

in GB 1,528,384. More recently, studies on the use of sulphur in bituminous mixtures have indicated that the use of sulphur-modified bitumen is feasible. Sulphur-modified bitumen is formulated by replacing some of the bitumen in conventional binders by elemental sulphur.

One of the problems encountered when using sulphur in bitumen is the unwanted formation of H_2S , resulting from dehydrogenation reactions between bitumen and sulphur at high temperatures.

Even low H_2S emission from sulphur-comprising asphalt, meaning asphalt formulated using sulphur-modified bitumen wherein elemental sulphur has been used to replace part of the bitumen, presents an emission nuisance on road paving projects. This is due to the gradual H_2S gas concentration increase to high levels in the air voids in the loose paving mixture during storage in silos and during truck delivery to the paving site. The "stored" gas is released when the air pockets in the mixture are opened up as the mixture is dumped from the delivery trucks or as the mixture is subjected to mechanical mixing.

In view of the substantial amounts of sulphur used, especially in sulphur-comprising asphalt having high sulphur-bitumen weight ratios, e.g. as high as 1:1, H_2S emission is a serious problem. Therefore, it is necessary to reduce the unwanted formation and emission of H_2S from sulphur-comprising asphalt.

One method to reduce H_2S -emission from hot cast sulphur-asphalt mixtures is to add an H_2S -suppressant in the process to manufacture sulphur-bitumen mixtures by mixing and heating sulphur and bitumen in the presence of added H_2S -suppressant as described in US 3,960,585.

A disadvantage of the method described in US 3,960,585 is that liquid H₂S-suppressant has to be injected into paving mixture at the mixing plant. Consequently, equipment for injecting has to be set up and maintained at the mixing plant, making the process cumbersome and costly. Another disadvantage is that it is more difficult to achieve a homogeneous distribution of H₂S-suppressant in the paving mixture, as a relatively small amount of liquid H₂S-suppressant is added to a relatively large mixture of solids and liquids.

SUMMARY OF THE INVENTION

It has now been found that sulphur pellets comprising H₂S-suppressant can be successfully used in a process for the manufacture of a sulphur-comprising asphalt paving mixture.

The invention provides a sulphur pellet comprising at least one H₂S-suppressant. The sulphur pellet according to the invention offers the advantage that when it is used in any process where the aim is to achieve a suppression of H₂S formation or emission, the efficiency of the H₂S-suppressant will be higher because the H₂S-suppressant will already be close to the source of H₂S formation, namely the sulphur.

The invention further provides a process for the manufacture of sulphur pellets according to the invention, the process comprising the steps of:

- (a) mixing elemental sulphur, one or more H₂S-suppressants and optionally a filler in a mixing unit to obtain a mixture;
- (b) shaping and/or pelletising the mixture obtained in step (a) in a pelletising unit to obtain H₂S-suppressant-comprising sulphur pellets.

The invention also provides a process for the manufacture of a sulphur-comprising asphalt paving mixture using H₂S-suppressant comprising sulphur pellets according to the invention. The process comprises the steps of:

(i) preheating bitumen at a temperature of between 140 and 180 °C;
(ii) preheating aggregate at a temperature of between 140 and 180 °C;

(iii) mixing the hot bitumen with the hot aggregate in a mixing unit,

wherein sulphur pellets comprising H₂S-suppressant according to the invention are added in at least one of the steps (i), (ii) or (iii), preferably in step (iii).

The use of sulphur pellets according to the invention offers the advantage that the H₂S-suppressant is more homogeneously incorporated in the sulphur-comprising asphalt paving mixture because the H₂S-suppressant is added as part of one of the constituents, instead of adding a relatively small amount of liquid H₂S-suppressant to a relatively large mixture of solids and liquids.

An even more important advantage is that in the resulting sulphur-comprising asphalt paving mixture, the H₂S-suppressant will be in the vicinity of the sulphur as the H₂S-suppressant was incorporated in the sulphur pellets. The efficiency of the H₂S-suppressant will therefore be higher, as explained before.

The invention also provides the use of a sulphur-comprising asphalt paving mixture comprising H₂S-suppressant in the paving of roads.

DETAILED DESCRIPTION OF THE INVENTION

The term "bitumen-aggregate" will be used interchangeable with the term "asphalt". The term "bitumen" as used herein refers to a binder.

Reference herein to pellets is to any type of formed sulphur. Formed sulphur is elemental sulphur that has been cast from the molten state into some kind of regularly sized particle, for example flakes, slates or sphere shaped sulphur such as prills, granules, nuggets and pastilles or half pea sized sulphur.

Typically, the sulphur pellet comprises in the range of from 60 to (and including) 100 wt%, preferably from 75 to (and including) 100 wt% and more preferably from 90 to (and including) 100 wt% of elemental sulphur, based on the total weight of the pellet.

Reference herein to an H₂S-suppressant is to a compound capable of suppressing the formation or emission of H₂S. Typical H₂S-suppressants are compounds selected from the class of free radical inhibitors and redox catalysts. Preferred H₂S-suppressants are selected from the group of tetra-alkyl-thiuram disulfide, dithiocarbamates, especially zinc dialkyl dithiocarbamates, amine compounds, iodine, copper salts, copper oxides, cobalt salts, cobalt oxides, iron oxides and iron salts.

Preferred iron salts are iron chloride compounds, in particular those iron chloride compounds selected from the group of ferric chloride, hydrated ferric chloride, ferrous chloride and hydrated ferrous chloride. Hydrated ferrous chloride is the most preferred, because of its greater effectiveness as an H₂S-suppressant and because of its non-corrosivity.

The sulphur pellet comprising H₂S-suppressant according to the invention typically comprises H₂S-

suppressant in amounts in the range of from 0.02% to 10% (w/w), preferably from 0.05% to 6.5%, more preferably from 0.1% to 2.0%, based on the total pellet.

Typically, the H₂S-suppressant is distributed
5 homogeneously throughout the sulphur pellet.

The formation of H₂S originates from sulphur. An important advantage of the sulphur pellets comprising H₂S-suppressant according to the invention is that because the H₂S-suppressant is added as an integral part
10 of the sulphur pellet, suppression of H₂S formation will be more efficient because the H₂S-suppressant will be located in the vicinity of the source for H₂S formation, namely sulphur.

The invention further provides a process for the
15 manufacture of sulphur pellets according to the invention. In step (a) of the process for the manufacture of H₂S-suppressant-comprising sulphur pellets according to the invention, elemental sulphur is mixed with one or more H₂S-suppressants and optionally a filler in a mixing
20 unit to obtain a mixture.

Preferred H₂S-suppressants are compounds selected from the class of free radical inhibitors and redox catalysts as hereinbefore described. Preferably, the H₂S-suppressant is added as a solution in a suitable solvent,
25 more preferably as a concentrated solution in a suitable solvent. Typically, the solvent is water. Typically, the H₂S-suppressant solution is introduced by pumping the solution from a reservoir unit into the mixing unit.

Typically, the mixing takes place at atmospheric
30 pressure and at elevated temperatures. The mixing can take place at temperatures between 100 °C and 130 °C, preferably between 115 °C and 121 °C or at least 113 °C.

Elemental sulphur can be introduced into the mixing unit in many ways. Suitably it is added as sulphur powder, or as a flow of molten sulphur or as a slurry of water and sulphur particles.

5 In one preferred process, the elemental sulphur is introduced as a slurry of water and sulphur particles. Typically, the sulphur particles are dispersed or suspended in the slurry. Preferably, the particles have a size ranging from between about 0.5 to about 150 microns, preferably between about 1.0 and about 100 microns. To
10 avoid the removal of excess water at a later stage in the process, the water content in the sulphur slurry is typically kept as low as possible, preferably between approximately 10 and 40% based on the total weight of the mixture, more preferably between 15 and 30% based on the
15 total weight of the slurry. In the case where the sulphur particles are suspended in the slurry, the sulphur slurry is preferably stirred or mixed in a suitable apparatus to homogenise the slurry prior to introducing it into the
20 manufacturing process.

In a preferred embodiment, the sulphur slurry contains sulphur particles which are dispersed in the water. This type of slurry, henceforth referred to as dispersed or emulsified sulphur slurry, comprises
25 dispersed sulphur particles in water, preferably dispersed micron-sized sulphur particles in water. The sulphur particles are suitably kept in dispersion through the addition of a suitable emulsifier. Suitable emulsifiers are known in the art and are not critical to
30 the invention. An advantage of using dispersed sulphur particles is that the precipitation of sulphur particles is kept to a minimum and the sulphur is distributed more homogeneously throughout the water. Thus, the need for

stirring or mixing prior to introducing the sulphur slurry into the reactor unit is reduced. Typically, the slurry is introduced by pumping the slurry from a sulphur slurry reservoir unit into the reactor unit. Preferably, the slurry is stirred or mixed in a suitable apparatus before it is introduced into the mixing unit of step (a).

In another preferred process, the elemental sulphur is introduced into the reactor unit in step (a) as molten sulphur. Molten sulphur can be obtained from solid sulphur, by melting in a suitable melting apparatus, for instance a tube melter.

The use of molten sulphur is advantageous when sulphur is obtained in the molten state from an industrial process. Processes for the removal of unwanted sulphur components from natural gas usually produce sulphur in the molten state and the use of this molten sulphur directly in the sulphur pellet producing process avoids the need for additional steps, such as drying and grinding of the sulphur, to obtain a sulphur slurry. An additional advantage of using molten sulphur is that no additional water is introduced into the process. When adding elemental sulphur in the molten state, the temperature of the sulphur-comprising mixture is preferably kept above the melting point of sulphur, preferably between temperatures of 115 °C and 121 °C, to ensure that the sulphur is kept in the molten state.

In yet another preferred process, biologically produced elemental sulphur is used. Reference herein to biologically produced elemental sulphur is to sulphur obtained from a process wherein sulphur-comprising components, such as sulphides or H_2S , are converted to elemental sulphur via biological conversion. Biological conversion can suitably be effected using sulphide-

oxidising bacteria. Suitable sulphide-oxidising bacteria can be selected for instance from the known autotrophic aerobic cultures of the genera *Thiobacillus* and *Thiomicrospira*. An example of a suitable biological conversion process to obtain the biologically produced elemental sulphur suitable for the process according to the invention is the process for the removal of sulphur compounds from gases wherein the gas is washed with an aqueous washing liquid and the washing liquid is subjected to sulphide-oxidising bacteria, as described in WO 92/10270. Biologically produced elemental sulphur has a hydrophilic nature. An advantage of biologically produced elemental sulphur is that fouling or blocking of equipment is substantially reduced or even eliminated due to the hydrophilic nature. The biologically produced elemental sulphur can be introduced into the process as solid sulphur, as a slurry (including dispersed or emulsified sulphur) or as molten sulphur.

To achieve a more homogeneous distribution of the H_2S -suppressant throughout the sulphur, the H_2S -suppressant and the elemental sulphur are preferably premixed and introduced as a slurry or as a liquid into the mixing unit of step (a).

Optionally, a filler can be added in step (a). Suitable fillers include mineral fillers, such as calcium-based mineral fillers (for example calcium hydroxide). The addition of mineral fillers enables the use of a smaller quantity of sulphur and helps to improve the temperature-stability of the pellets.

Suitably, the amount of filler in the pellet is in the range of from 0.1 to 30 % (w/w), preferably from 0.5 to 20%, more preferably from 1 to 10%, based on the total weight of the pellet.

After step (a), a mixture comprising sulphur, one or more H₂S-suppressants and optionally a filler is obtained. This mixture is shaped and/or pelletised in a pelletising unit in step (b) to obtain H₂S-suppressant comprising pellets.

Suitable pelletising units are units for the formation of granules or pellets as described in Perry's Chemical Engineers' Handbook, chapter 20 (1997) or units wherein a liquid mixture comprising sulphur can be sprayed or poured onto a surface so that sulphur pellets are formed after cooling, for example as described in US 4,081,500 or US 4,043,717. The pelletising unit can suitably comprise a granulator, preferably a drum granulator, or a rotating drum or a device for spraying molten sulphur.

In a preferred process, the mixture comprising sulphur and H₂S-suppressant is liquid, the elemental sulphur being in the molten state.

In one preferred embodiment, the pelletising unit comprises a rotating drum. In this embodiment, the liquid mixture comprising sulphur and H₂S-suppressant and optionally a filler obtained after step (a) is cooled and solidified on the outside of a rotating drum. The cooled mixture peels off the rotating drum into flakes, the flakes being the sulphur pellets comprising an H₂S-suppressant.

In another preferred embodiment, the pelletising unit comprises a means for transporting and the pelletising is done by forming droplets of the liquid mixture obtained after step (a) and depositing these droplets onto the means for transporting, for example a conveyor belt. Suitably, the liquid mixture is sprayed onto a conveyor belt through a spray head. After cooling, the

droplets form into pellets.

In yet another preferred embodiment, the pelletising unit comprises a granulator and the pelletising is done by applying successive coats of a liquid mixture
5 obtained after step (a) to solidified particles of a mixture obtained after step (a). The coating is suitably performed until the resulting pellet reaches the desired diameter. Typically, the liquid mixture obtained after step (a) is sprayed into the granulator, thereby coating
10 the solidified particles.

In yet another preferred embodiment, the pelletising unit comprises a spraying device and sulphur pellets are formed by spraying the liquid mixture obtained after
15 step (a) into a tank containing water, thereby cooling the liquid mixture into pellets. Alternatively, the liquid mixture obtained after step (a) is sprayed from the top of a tower against an upward flow of air thereby cooling into pellets.

Optionally, H₂S-suppressant-comprising sulphur
20 pellets obtained after step (b) are dried, suitably air-dried or dried in a drying unit. Suitable drying units include drying units wherein heat transfer for drying is accomplished by direct contact between the wet solid and hot gases. Typically, the drying unit is a rotary dryer.

25 The invention further provides a process to manufacture a sulphur-comprising bitumen-aggregate mixture, also referred to as sulphur-comprising asphalt.

In step (i) of this process bitumen is heated, typically at a temperature of between 120 and 180°C,
30 preferably between 130 and 150 °C, more preferably between 140 and 150 °C.

In step (ii) of this process aggregate is heated, typically at a temperature of between 120 and 180°C,

preferably between 130 and 150 °C, more preferably between 140 and 150 °C

In step (iii), the hot bitumen and hot aggregate are mixed in a mixing unit. Typically, the mixing takes place at a temperature of between 120 and 180°C, preferably between 130 and 150 °C, more preferably between 140 and 150 °C. Typically, the mixing time is between 10 and 60 seconds, preferably between 20 and 40 seconds.

Sulphur pellets comprising H₂S-suppressant are added in at least one of the steps (i), (ii) or (iii).

Preferably, the addition of sulphur pellets comprising H₂S-suppressant is followed by mixing for an additional time. Typically, the additional mixing time is between 5 and 600, preferably between 10 and 100 seconds.

In a preferred embodiment, hot aggregate is mixed with H₂S-suppressant comprising sulphur pellets. Hot bitumen is then added to the hot aggregate-sulphur mixture.

In another preferred embodiment, hot aggregate is mixed with hot bitumen and the H₂S-suppressant comprising sulphur pellets are added to the hot bitumen-aggregate mixture. This embodiment offers the advantage of producing a stronger sulphur-asphalt mix strength.

In yet another preferred embodiment, hot bitumen is mixed with H₂S-suppressant comprising sulphur pellets and the resulting hot bitumen-sulphur mixture is mixed with hot aggregate to obtain a sulphur-comprising asphalt mixture.

Typically, the amount of sulphur pellets comprising H₂S-suppressant added to the bitumen-aggregate (asphalt) mixture is such, that a mixture comprising sulphur and

bitumen in a weight ratio from about 1:0.5 to 1:5, preferably from about 1:1 to 1:4, is obtained.

Typically, the bitumen/aggregate mixture comprises at least 2 weight% of bitumen, based on the total weight of the mixture. Mixtures comprising from about 1 weight% to about 10 weight% of bitumen are preferred, with a special preference for mixtures comprising from about 3 weight % to about 6 weight % of bitumen based on the total weight of the mixture.

The sulphur-comprising asphalt paving mixture thus obtained can be used in the paving of roads, for example by applying it to the road with a paving machine, typically followed by roller compaction until the required density has been reached.

The use of sulphur pellets comprising H_2S -suppressant eliminates the need for the installation and maintenance of injecting equipment at an bitumen-aggregate mixing plant, thereby offering advantages compared with the process wherein H_2S -suppressant are added separately.

Another advantage is that the sulphur pellets comprising H_2S -suppressant according to the invention may help to prevent the detachment of bitumen film, the so-called "stripping", from water-sensitive mineral aggregates. This is especially important when hydrated lime is added to asphalt mixtures. The addition of hydrated lime to asphalt mixtures is beneficial because it reacts with bitumen, thereby removing oxygen-comprising bitumen components and forming a strong bond. In sulphur comprising asphalt mixtures however, the addition of hydrated lime causes problems. Some of the lime may be in the CaO state and a reaction with sulphur can take place to form synthetic gypsum. This synthetic gypsum is water-soluble and can cause sulphur-bitumen-

aggregate disintegration in the presence of water. The sulphur-pellets comprising H_2S -suppressant according to the invention solve this problem as the H_2S -suppressant delays bitumen-aggregate disintegrating and can prevent disintegrating from mineral aggregates.

Yet another advantage of the sulphur-pellets according to the invention is that because the H_2S -suppressant is incorporated in the sulphur pellet, the H_2S -suppressant will be in the vicinity of the sulphur in the final asphalt mixture, thereby being able to suppress the formation of H_2S evolving from the sulphur before the H_2S is released.

EXAMPLE 1 (comparative)

A mixture was prepared with the following procedure. Aggregate and bitumen were heated in an oven to 165 °C. The bitumen was added to the aggregate and mixed for 30 seconds in a Hobart mixer. Elemental sulphur pastilles without added H_2S suppressant were added and mixed for an additional 150 seconds. The temperature of the mixture was approximately 145 °C after mixing.

Approximately 3700 grams of mixture, with the following composition: Aggregate: 3535 g; bitumen: 132 g (3.5%); elemental sulphur: 87 g (2.3%), were then poured into a thermostatically controlled heated vessel.

H_2S concentrations in the vessel were measured periodically, approximately 30 mm above the surface of the mixture, with a gas meter with a built-in pump for drawing the H_2S gas into the meter. Measurements were done (a) after initial mixing and at various time periods subsequently, after sulphur-comprising asphalt re-mixing manually with the vessel cover removed and (b) after various time periods with the cover placed on the vessel,

to force the gas concentration to accumulate within the vessel.

The mixture was stirred thoroughly from time-to-time and then a cover was placed on the vessel for a short period of time, typically 5 minutes, to allow the H₂S gas to accumulate inside the vessel. The H₂S concentration was then measured at 5 minute intervals. The H₂S concentration was found to be 37 ppm after 5 minutes, at a mix temperature of 145 °C.

EXAMPLE 2 (according to the invention)

A mixture was prepared using the procedure described in the comparative example, except that H₂S-suppressant comprising sulphur pellets, with a H₂S-suppressant concentration of 6.5% based on the total pellet, were used.

The resulting mixture had the following composition: Aggregate: 3535 g; bitumen: 132 g (3.5% based on total mix weight); elemental sulphur: 87 g (2.3% based on total mix weight), plus 6 g ferric chloride (hydrated weight 20 g). The H₂S concentration was found to be between 14 and 20 ppm after 5 minutes at a mix temperature of 149 °C.

The results clearly show that the use of sulphur pellets comprising H₂S suppressant results in a substantial decrease of H₂S formation.

C L A I M S

1. Sulphur pellet comprising an H₂S-suppressant.

2. Sulphur pellet according to claim 1, comprising in the range of from 60 to 100 wt% elemental sulphur, based on the total weight of the pellet.

5 3. Sulphur pellet according to claim 1 or 2, wherein the H₂S-suppressant is one or more compounds selected from the class of free radical inhibitors and redox catalysts.

10 4. Sulphur pellet according to any one of claims 1 to 3, wherein the H₂S-suppressant is selected from the group of iodine, amine compounds, copper salts, copper oxides, iron salts, iron oxides, cobalt salts and cobalt oxides.

15 5. Sulphur pellet according to claim 4, wherein the iron salts are iron chloride compounds, preferably selected from the group of ferric chloride, hydrated ferric chloride, ferrous chloride and hydrated ferrous chloride.

20 6. Sulphur pellet according to any one of claims 1 to 5, comprising H₂S-suppressant in amounts in the range of from 0.02% to 10% (w/w), preferably from 0.05% and 6.5%, more preferably between 0.1% to 2.0%, based on the sulphur pellet.

7. A process for the manufacture of sulphur pellets comprising at least one H₂S-suppressant, the process comprising the steps of:

25 (a) mixing elemental sulphur, one or more H₂S-suppressants and optionally a filler in a mixing unit to obtain a mixture;
(b) shaping and/or pelletising the mixture obtained in

step (a) in a pelletising unit to obtain H₂S-suppressant-comprising sulphur pellets.

8. A process as claimed in claim 7, wherein the elemental sulphur is introduced as molten sulphur, the temperature of the mixture preferably being kept above 113 °C.

9. A process as claimed in claim 7 or 8, wherein the H₂S-suppressant is one or more compounds selected from the class of free radical inhibitors and redox catalysts.

10. A process to manufacture a sulphur-comprising asphalt paving mixture, the process comprising the steps of:

(i) preheating bitumen at a temperature of between 140 and 180 °C;

(ii) preheating aggregate at a temperature of between 140 and 180 °C;

(iii) mixing the hot bitumen with the hot aggregate in a mixing unit,

wherein sulphur pellets comprising H₂S-suppressant

according to any one of claims 1 to 6 are added in at least one of the steps (i), (ii) or (iii), preferably in step (iii).

11. A sulphur-comprising asphalt paving mixture comprising H₂S-suppressant, obtainable by a process according to claim 10.

INTERNATIONAL SEARCH REPORT

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A. CLASSIFICATION OF SUBJECT MATTER
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According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
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Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EP0-Internal, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 3 960 585 A (GAW ET AL) 1 June 1976 (1976-06-01) cited in the application column 1, line 40 - column 2, line 62 abstract; claims 1-17; examples 1,2	1-11
X	US 2003/073761 A1 (BUTLER JAMES R ET AL) 17 April 2003 (2003-04-17) paragraph '0025! - paragraph '0039! abstract; claims 1-42	1-11
X	GB 2 384 240 A (* SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V.) 23 July 2003 (2003-07-23) page 3, line 6 - page 4, line 18 abstract; claims 1-9; examples A,B	1-11
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Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

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